



Supplement of

A halocarbon survey from a seagrass dominated subtropical lagoon, Ria Formosa (Portugal): flux pattern and isotopic composition

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11 Design of cryotrap used for air and seawater samples (Purge and trap)

2The analytic procedure is based on the method of Bahlmann et al. (2011) for the isotopic
3determination of trace gases with some adjustments. We changed the design of the cryotrap
4in order to establish a better temporal resolution by reducing the sample preparation/analysis
5time. The self-made cryotrap was 1/4" siltek capillary (40 cm) connected to a stainless steel
6capillary (60 cm) and were bowed forming a U-shape. This allows the cryotrap being easily
7submersed in the dry shipper (Voyageur 12, Air Liquide, Germany) as cooling source during
8sampling. The cryotrap was filled with Tenax TA (20-35 mesh, 5 cm, Grace, Deerfield,
9USA) at the lower end of 1/4" capillary and fixed with silanized glass wool at the top and
10bottom of the packing material. The inlet and outlet were capped with Swagelok fittings and
11endcaps allowing rapid connection and closure before/after sampling and measurements.

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132 Measurement of air and seawater samples

14The instrumental set up is shown in Fig. S1. After sampling (air sampling or purge&trap of
15water samples), the samples were thermally desorbed from the cryotrap (310°C) under a flow
16of high-purity helium (50 mL min⁻¹, 99.999%, Linde, Germany) for 15 min (red lines/arrows).
17The analytes were re-trapped on peltier-cooled sampling tubes (Bahlmann et al., 2011) at
18-15°C using a Valco eight port valve (VICI, Valco instruments, Houston, USA). After sample
19transfer, the valco valve was switched and analytes were thermally desorbed (330°C) from the
20adsorbent tubes in counter-flow direction (He, 30 mL min⁻¹), here indicated as green
21lines/arrows. During the desorption (20 min), the analytes were then refocused on a cryotrap
22(quartz capillary, 60 cm, 0.32 i.d.) submerged in liquid nitrogen. The refocusing of analytes
23and injection into the GC-MS system proceeds using a second eight port valco valve. After
24retrapping, the valve is switched and compounds are sent to the GC-MS system in
25counterflow direction (black (dotted) lines/arrows) under ambient temperature. Due to high
26water amounts in air and water samples, the water was removed by two Nafion dryers (in
27silica gel), each after thermal desorption from the cryotrap and the adsorbent tubes.

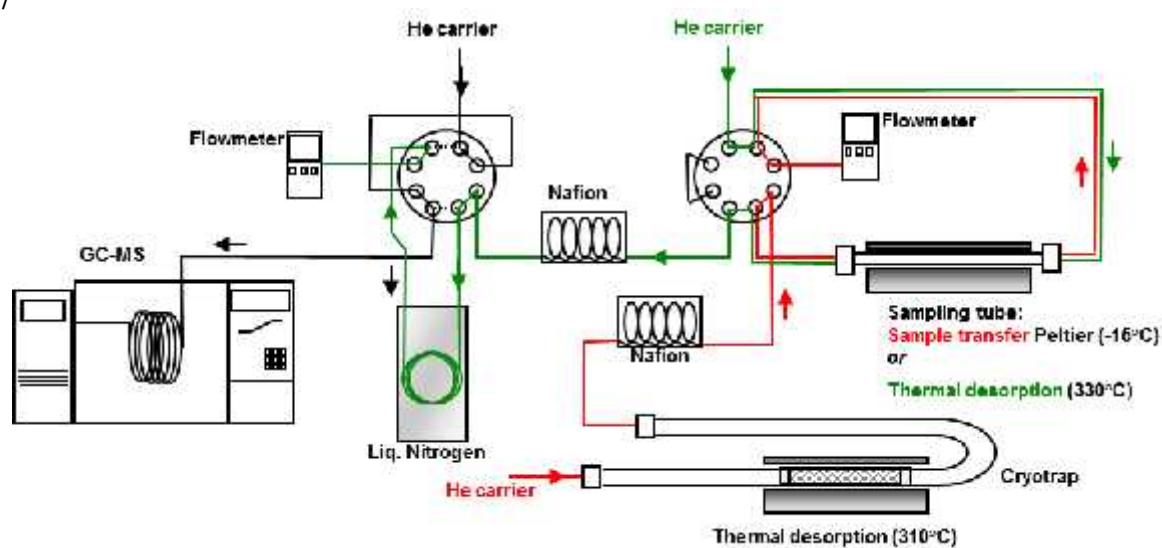
28The GC-MS (6890N/5975B, Agilent, Waldbronn, Germany) was equipped with a CP-
29PorabondQ column (25 m, 0.25 µm i.d., Varian). The flowrate was set to 3 mL. The oven
30temperature program was as follows: 40 °C, hold 4 min; 12° C min⁻¹ to 200°C, hold 2 min,
3118° C min⁻¹ to 240°C; 30° C min⁻¹ to 280°C, hold 5 min. The MS was operated in the electron

1 impact mode at 70 eV. Temperatures of quadrupole, source, and transfer line were 150°C,
 2 2230°C, and 250°C. Acquisition was executed in full scan mode (33-300 u). Target analytes
 3 were identified by their retention times and respective mass spectra and quantified using their
 4 major mass fragments. Quantification of CH₃Cl, CH₃Br, and CHBr₃ of air and water samples
 5 was done by using aliquots of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen, Sigma
 6 Aldrich, Germany). During on-site measurements, CH₃I was quantified by using the response
 7 factor against CH₃Br. Prior to the campaign, equivalent amounts of CH₃I and CH₃Br from
 8 single gas standards were analysed together for the response factor calculation.

9 The trapping and desorption efficiency (recovery rates) of the cryotrap was tested (n=4).
 10 2 mL of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen) and 20 µL CH₃I (100 ppm
 11 in nitrogen) was injected to the cryotrap submerged in the dry shipper using a stream of helium.
 12 Simulating “real” air sampling, helium was stream was set to 1 L min⁻¹ for 30 min (resulting in
 13 30 L). The whole sample treatment procedure was applied as described above. The mean
 14 recovery rates of a suite of halocarbons were 96% ranging from 93± 4% (CH₃Br) and 93±
 15 10% (CCl₄) to 100± 4% for CHBr₃. Individual recovery rates are displayed in Fig. S2.

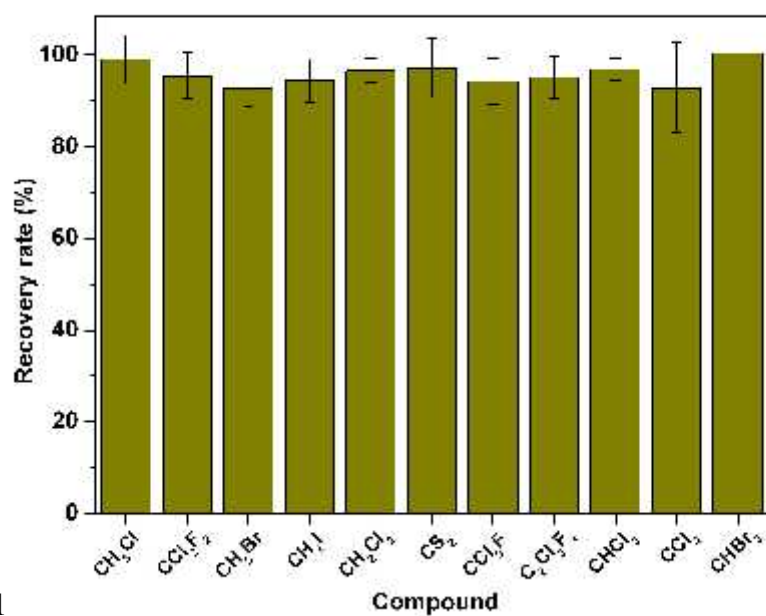
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18 Fig. S1: Scheme of the analytical system for the determination of halocarbons from air and
 19 water samples.

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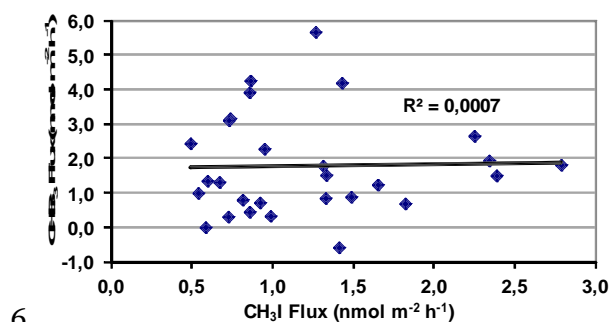
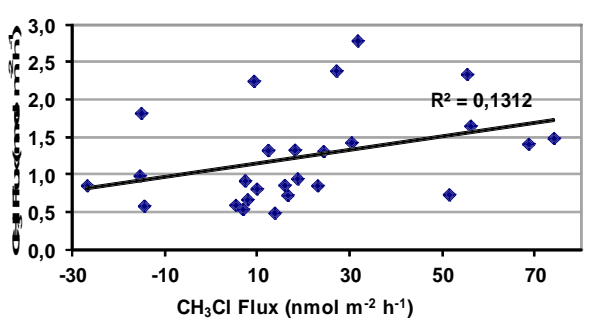
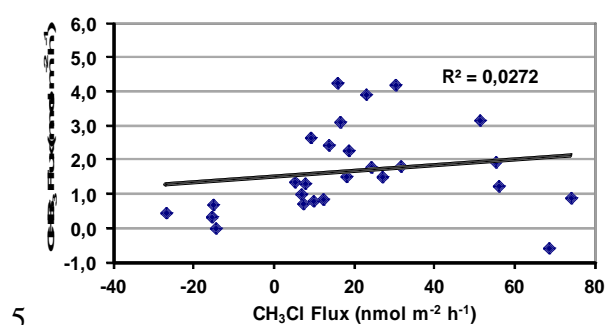
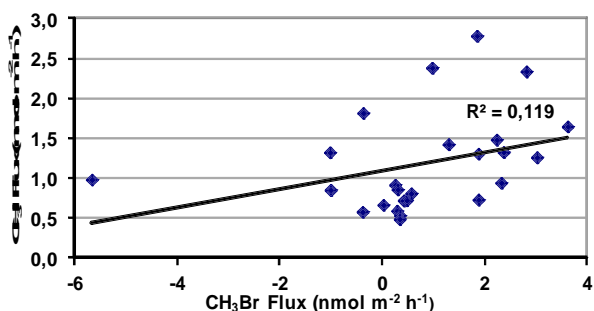
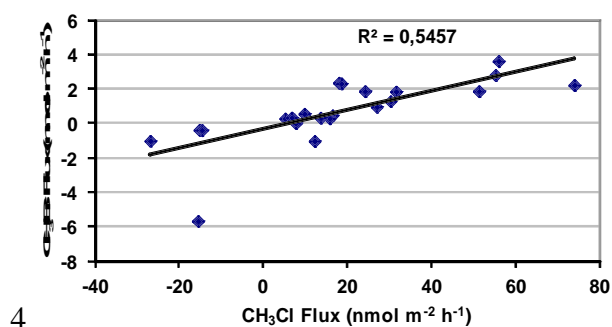
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2Fig. S2: Mean recovery rates and their absolute standard deviations of halocarbons from
3recovery experiments (n=4).

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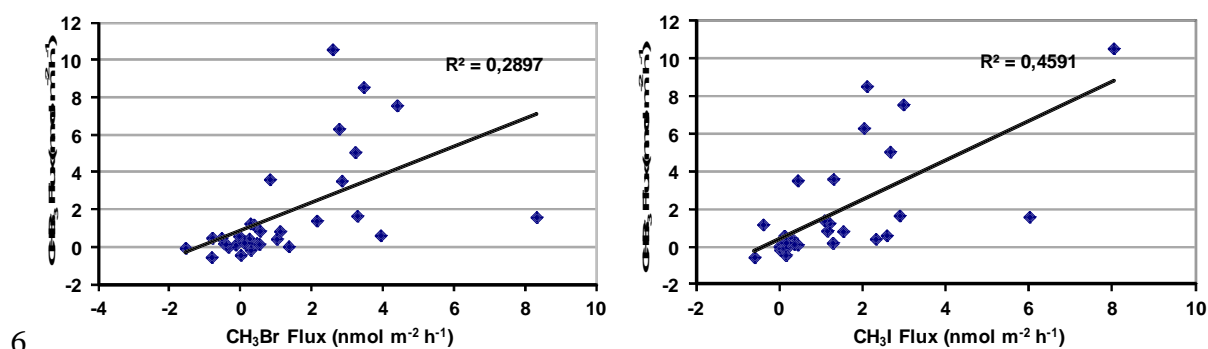
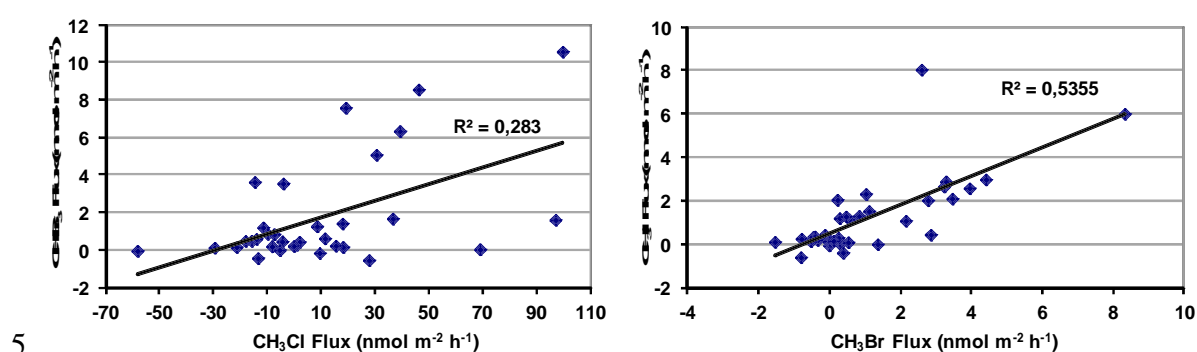
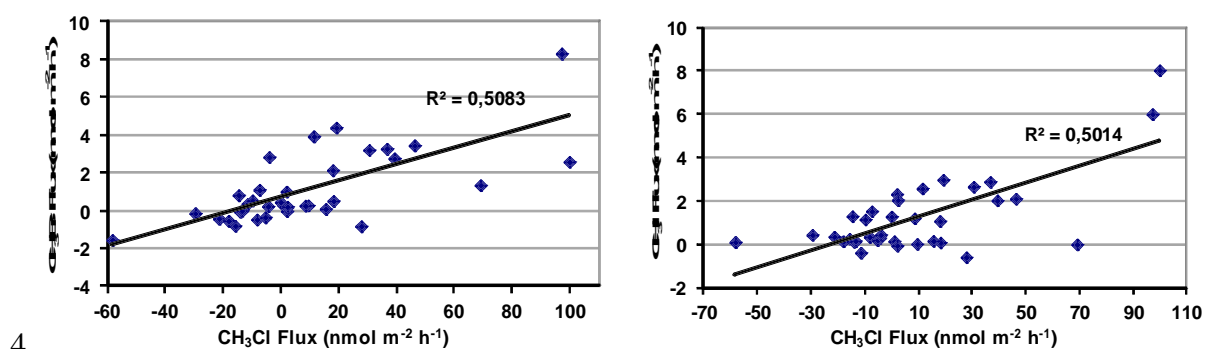
13 Correlation scatter plots of halocarbon fluxes from seagrass meadows

2Correlation scatter plots of halocarbon fluxes from seagrass meadows during the summer
3campaign in 2011. Data refers to measurements obtained from air-exposed seagrass meadows.

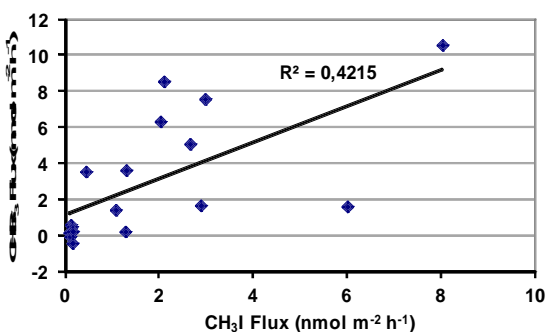
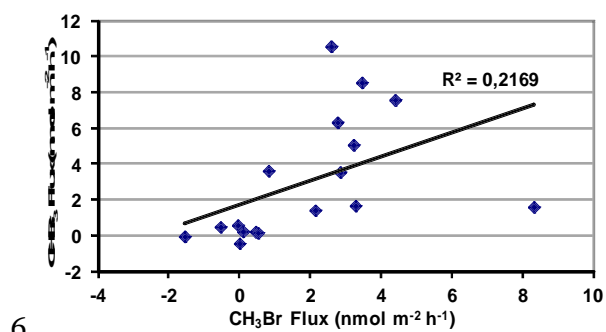
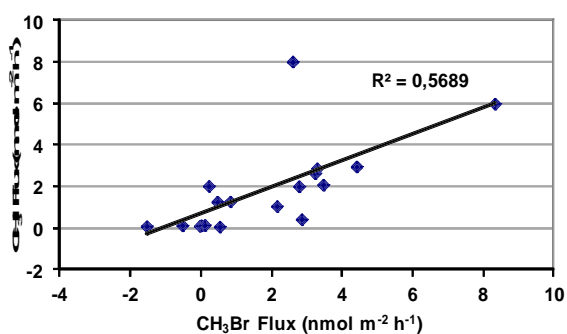
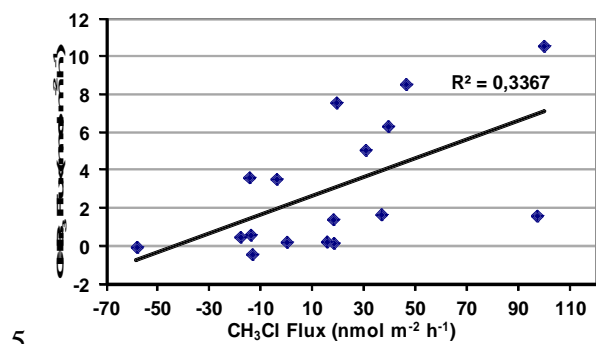
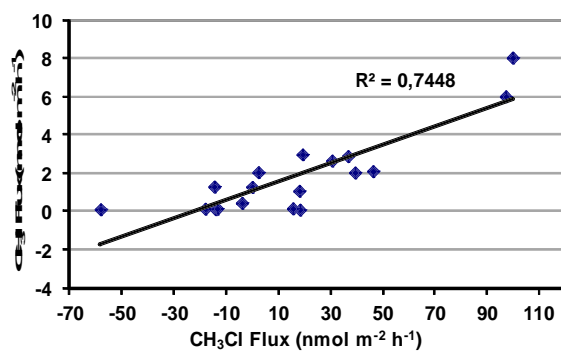
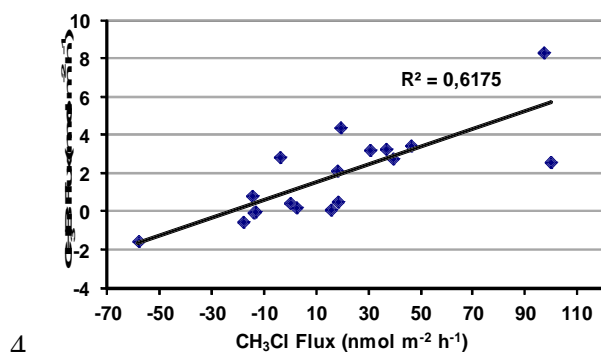


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1Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring
 2campaign in 2012. Data refers to measurements obtained from air-exposed and submerged
 3seagrass meadows.

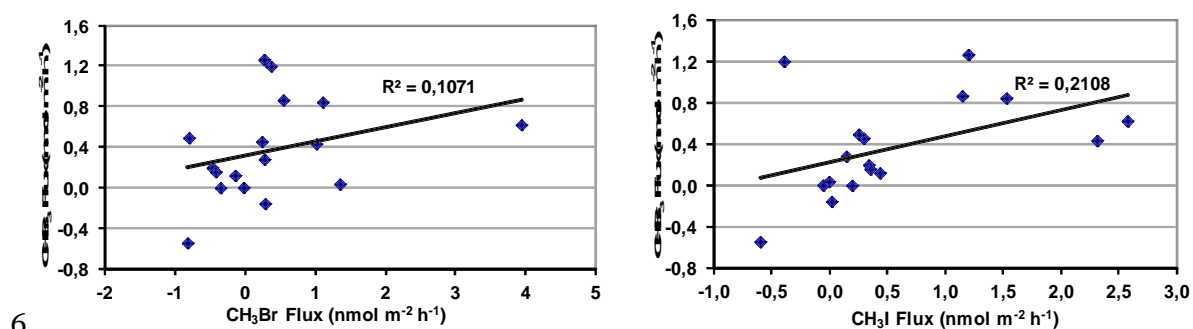
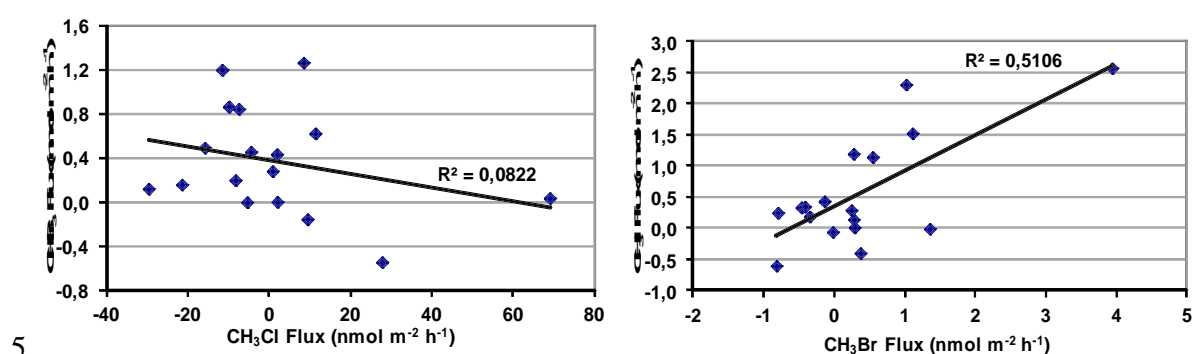
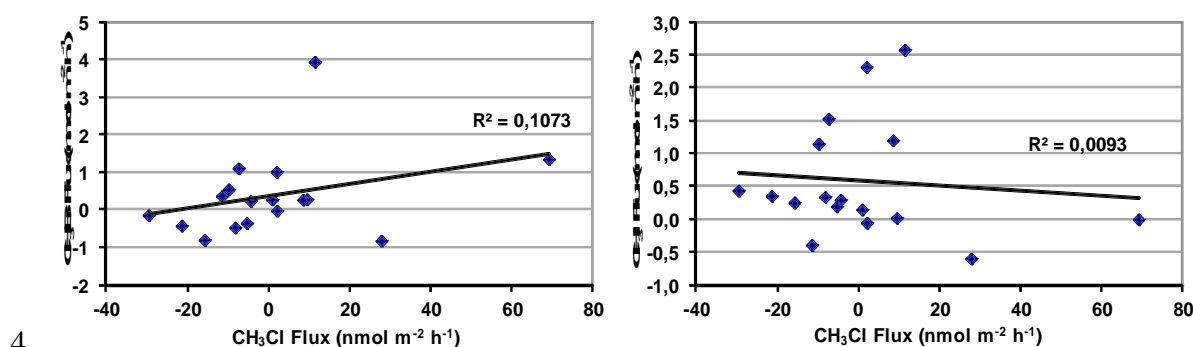


1Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring
 2campaign in 2012. Data refers to measurements obtained from submerged seagrass meadows,
 3only.



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1Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring
2campaign in 2012. Data refers to measurements obtained from air-exposed seagrass meadows,
3only.



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8References

9Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis, W.: A high volume sampling system for
10isotope determination of volatile halocarbons and hydrocarbons, Atmos. Meas. Tech., 4, 2073-2086,
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